

## $^{51}\text{V}$ NMR Study of $\text{VOCl}_3$ Immobilized on the $\text{SiO}_2$ and $\text{MgCl}_2$ Surface

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**Abstract**—The magnetic shielding tensor and quadrupole interaction parameters, as well as the mutual orientation of tensors for the  $(\equiv\text{SiO})\text{VOCl}_2$  complex obtained by the immobilization of  $\text{VOCl}_3$  on the  $\text{SiO}_2$  surface are determined. The state of  $\text{VOCl}_3$  on the surfaces of  $\text{MgCl}_2$  and modified  $\text{SiO}_2$  with all surface OH groups replaced by Cl atoms is studied. To prepare the modified  $\text{SiO}_2$ ,  $\text{CCl}_4$  and  $\text{SiCl}_4$  are used as chlorinating agents. The formation of structurally similar pentavalent vanadium complexes on the surface of these supports is shown. A model for the coordination environment of vanadium on the chlorine-containing supports is proposed. The vanadium atom exists in the distorted pentahedral environment and is bound to the support through either two chlorine atoms or chlorine and oxygen atoms. A correlation between the coordination of  $\text{VOCl}_3$  and catalytic properties of  $\text{VOCl}_3/\text{MgCl}_2$  is assumed.

### INTRODUCTION

Currently, polyolefins are synthesized in the presence of Ziegler–Natta catalysts. Supported titanium–magnesium catalysts (TMC) containing titanium tetrachloride as an active component supported on highly dispersed magnesium chloride are the best known among these systems. Several papers devoted to supported vanadium–magnesium catalysts (VMC) for ethylene polymerization containing vanadium compounds ( $\text{VCl}_4$  and  $\text{VOCl}_3$ ) as an active component instead of titanium chloride have been published in recent years [1–10]. These catalysts possess several interesting properties: (1) in the presence of VMC, unlike TMC, polyethylene with a broad molecular-weight distribution is formed [4, 8, 11] and (2) VMC possess a higher copolymerization activity as compared to that of TMC in ethylene copolymerization with  $\alpha$ -olefins [4, 12, 13].

The authors of [3] reported that titanium tetrachloride in TMC, vanadium tetrachloride and vanadium hydroxytrichloride in VMC interact with the same sites of the support, specifically with highly dispersed magnesium chloride. These sites are assumed to be the surface coordinatively unsaturated magnesium ions with chlorine vacancies [14–17]. These magnesium ions have the properties of Lewis acids [18–20].

Recently, nuclear magnetic resonance in solids has been recognized as a method that is the most sensitive to fine details of the local nuclear environment. In the case of vanadium,  $^{51}\text{V}$  NMR spectroscopy reliably determines the type of the coordination environment of vanadium and the type of association of vanadium polyhedra. Therefore,  $^{51}\text{V}$  NMR spectroscopy was used

to study the structure of surface complexes of several catalysts [21–24].

In this work, we applied  $^{51}\text{V}$  NMR in solid to study the  $\text{VOCl}_3$  structure on the  $\text{MgCl}_2$  surface to compare it to the structures formed when  $\text{VOCl}_3$  was adsorbed on silica gel with different chemical compositions of the surface.

### EXPERIMENTAL

Vanadium hydroxytrichloride  $\text{VOCl}_3$  (a solution in  $\text{CCl}_4$ ) was distilled in a vacuum at  $20^\circ\text{C}$ . Silicon dioxide (Davison 952 trade mark,  $S_{\text{sp}} = 260 \text{ m}^2/\text{g}$ ) was calcined in a vacuum at  $260$ – $700^\circ\text{C}$ . Modified  $\text{SiO}_2$  was treated with chlorinating agents ( $\text{CCl}_4$  and  $\text{SiCl}_4$ ) at  $400^\circ\text{C}$  as described in [25].

The  $\text{Rb}_2\text{VOCl}_5 \cdot \text{H}_2\text{O}$  sample was prepared by a procedure described in [26].

Two samples of magnesium chloride were used. The first of them,  $\text{MgCl}_2$ -1, was prepared according to the procedure described in [27] from anhydrous crystalline magnesium chloride and activated using dry grinding for 10 h in a ball mill. The specific surface area of the sample was  $29 \text{ m}^2/\text{g}$ .

The second sample,  $\text{MgCl}_2$ -2, was prepared according to the procedure described in [27] by the reaction of powdered magnesium with  $\text{C}_4\text{H}_9\text{Cl}$  (a molar  $\text{C}_4\text{H}_9\text{Cl}/\text{Mg}$  ratio of 3) in heptane at  $98^\circ\text{C}$ . Under these conditions, nonsolvated butylmagnesium chloride formed at the first stage of the synthesis was chlorinated with excess  $\text{C}_4\text{H}_9\text{Cl}$  to form a powdered product containing 90%  $\text{MgCl}_2$  and 10% organic polymeric part with the composition  $(\text{CH}_{2.3})_n$ . The sample was washed

with heptane and dried in a vacuum at room temperature. The specific surface area of the sample was 155 m<sup>2</sup>/g.

VOCl<sub>3</sub> was supported on the SiO<sub>2</sub> surface from the gas phase at room temperature. Other vanadium catalysts were prepared according to [1, 11] by the interaction of solutions of VOCl<sub>3</sub> or VCl<sub>4</sub> in CCl<sub>4</sub> with a suspension of MgCl<sub>2</sub> or modified SiO<sub>2</sub> in heptane at 80°C and the molar ratio V : support = 0.05 : 0.1. The catalyst was repeatedly washed with heptane and dried in a vacuum.

The vanadium concentration was determined by flame absorption spectrophotometry on an AAS-1-N spectrometer.

The conditions of preparation and results of chemical analysis are presented in Table 1.

To obtain IR spectra, we used the specially constructed cell that allowed us to introduce the sample and measure IR spectra in a vacuum. Diffuse-reflectance IR spectra were recorded using an IFS-113V spectrometer (Bruker) equipped with a diffuse-reflectance attachment. The spectra are presented in the form of  $F(R)$ , where  $R$  is the reflection coefficient, and  $F(R)$  is the Kubelka–Munk function.

ESR spectra were recorded at 77 K at a frequency of 9.2–9.3 GHz using a Bruker ER-200D ESR spectrometer with 5-mm ampules. The modulation frequency of an ESR signal was 100 kHz, and the modulation amplitude was 0.5–1.0 mT. The MgO crystal with Mn<sup>2+</sup> and Cr<sup>3+</sup> admixtures was used as a standard for the determination of the  $g$ -factor of signals from the sample.

<sup>51</sup>V NMR spectra were obtained with a Bruker MSL-400 spectrometer (with a magnetic field of 9.4 T and a resonance frequency on vanadium  $\nu_0$  of 105.2 MHz). Experiments on quadrupole echo were

carried out by the two-pulse sequence:  $\{\pi/12(X) - t_1 - \pi/12(Y) - t_2\}$ , where  $t_1$  and  $t_2$  were empirically taken to be 55 and 57  $\mu$ s, respectively. Magic angle spinning (MAS) spectra were obtained at a rotation frequency of 10–15 kHz in silicon nitride rotors (with an external diameter of 5 mm) on a sensor designed by NMR Rotor Consult ApS (Denmark) [28]. The radio frequency pulse duration was  $\pi/12$  (which corresponded to 2  $\mu$ s for a highly powerful sensor and 1  $\mu$ s for a MAS sensor), and the delay between pulses varied from 0.1 to 10 s. Chemical shifts are presented relatively to VOCl<sub>3</sub> as an external standard. A sample was loaded into the rotor in inert chambers in argon, and then the sample in the rotor was flooded with paraffin. Then, the rotor was tightly closed with a cap with several rubber gaskets. Under these conditions, the sample remained unchanged for several days.

The SATRAS procedure (satellite transition spectroscopy, viz., detailed spectroscopy of rotation satellites) was used to analyze experimental data, that is, to determine in detail the magnetic shielding tensor and quadrupole interaction parameters and the mutual tensor orientation [29, 30].

The spectra were calculated by the unique NMR2 program developed by A.A. Shubin [31]. The program is partially based on the code of the NMR1 program [32] and uses (in the corresponding modification) an algorithm proposed in [33] for the fast calculation of the integral intensities of rotation satellites in MAS spectral of quadrupole nuclei. The program makes it possible to calculate the satellite intensities and the total NMR spectrum under the SATRAS conditions and estimate spin-Hamiltonian parameters from experimental intensities of rotation satellites. To simulate NMR spectra of samples with defects or strains in the lattice in the vicinity of the nucleus, we used the calcu-

**Table 1.** Conditions for the preparation of the samples, results of chemical analysis, and data on the catalytic properties (conditions for polymerization: the ethylene pressure is 3.8 atm,  $T = 80^\circ\text{C}$ , and the cocatalyst is triisobutylaluminum)

No.	Composition	Temperature of SiO <sub>2</sub> calcination, °C	Temperature of immobilization of vanadium compounds, °C	Concentration of vanadium, wt %	Catalyst activity*, (g PE/(g V) h atm) $\times 10^3$
1	VOCl <sub>3</sub> /SiO <sub>2</sub>	400	20	2.00	2.5
2	VOCl <sub>3</sub> /SiO <sub>2</sub> (CCl <sub>4</sub> )	280	60	0.11	–
3	VOCl <sub>3</sub> /SiO <sub>2</sub> (SiCl <sub>4</sub> )	700	80	0.16	1.8
4	VOCl <sub>3</sub> /MgCl <sub>2</sub> (1)	–	80	1.50	9.7
5	VOCl <sub>3</sub> /MgCl <sub>2</sub> (2)	–	20	0.90	48
6	VCl <sub>4</sub> /MgCl <sub>2</sub> (2)	–	20	1.10	74

\* PE is polyethylene.

lation of MAS NMR spectra with the distribution of different parameters of nuclei quadrupole interaction (NQI) and magnetic shielding (MS) tensors [34].

## RESULTS AND DISCUSSION

The initial VOCl<sub>3</sub> at room temperature is a liquid, whose <sup>51</sup>V NMR spectra exhibit a single line with a shift of 0 ppm. The spectrum of VOCl<sub>3</sub> vitrified at –173°C is a line with the axial anisotropy of the magnetic shielding tensor with the parameters presented in Table 2 [23, 35]. The high anisotropy value ( $\Delta\sigma \sim 500$  ppm) and close  $\sigma_1$  and  $\sigma_2$  values characterize the local environment of vanadium as a distorted tetrahedron with the axial symmetry (the symmetry axis is most likely directed along the V=O bond).

Highly active catalysts for ethylene polymerization are obtained when VOCl<sub>3</sub> is supported on the MgCl<sub>2</sub>-2 surface obtained by organomagnesium synthesis [1] (see row 5 in Table 1). Unfortunately, we failed to detect the NMR spectrum of the VOCl<sub>3</sub>/MgCl<sub>2</sub>-2 sample.

We studied in more detail the sample prepared by VOCl<sub>3</sub> adsorption on crystalline MgCl<sub>2</sub> activated by dry grind (MgCl<sub>2</sub>-1 support).

The large line width did not allow us to observe the <sup>51</sup>V NMR spectrum of VOCl<sub>3</sub>/MgCl<sub>2</sub>-1. Only the use of the MAS procedure with a rotation rate of 10–14 kHz and long scan accumulation ( $2-3 \times 10^5$ ) provide the desired result. The MAS <sup>51</sup>V NMR spectrum of the VOCl<sub>3</sub>/MgCl<sub>2</sub>-1 sample (curve 3) is shown in Fig. 1. The spectrum is a system of well-resolved lateral bands from the signal with the partially averaged chemical shift anisotropy. The detection of spectra with different rotation rates and analysis of lateral bands suggest that all vanadium atoms observed have the same local environment characterized by a magnetic shielding tensor anisotropy of  $\sim 600$  ppm and an isotropic shift of  $-470$  ppm (Table 2).

The absence of the NMR spectrum of the VOCl<sub>3</sub>/MgCl<sub>2</sub>-2 sample can possibly be due to the reduction of some vanadium ions when VOCl<sub>3</sub> is supported on the MgCl<sub>2</sub> surface. This is indicated by the ESR signal from paramagnetic V<sup>4+</sup> ions ( $g_{\parallel} = 1.957$ ,  $A_{\parallel} = 183$  mT,  $g_{\perp} = 1.985$ , and  $A_{\perp} = 69$  mT). The ESR

**Table 2.** Nuclear quadrupole interaction ( $C_Q, \eta_Q$ )\* and magnetic shielding tensor ( $\delta_{\sigma}, \eta_{\sigma}, \sigma_{\text{iso}}$ )\*\* parameters for the <sup>51</sup>V nucleus and Euler angles ( $\alpha, \beta, \gamma$ ), specifying the relative orientation of these two tensors for V<sup>V</sup> in the VO<sub>x</sub>/SiO<sub>2</sub> and VO<sub>x</sub>/MgCl<sub>2</sub> catalysts. The parameters were obtained by the SATRAS procedure and from the analysis of static and MAS <sup>51</sup>V NMR spectra at a frequency of 105.25 MHz

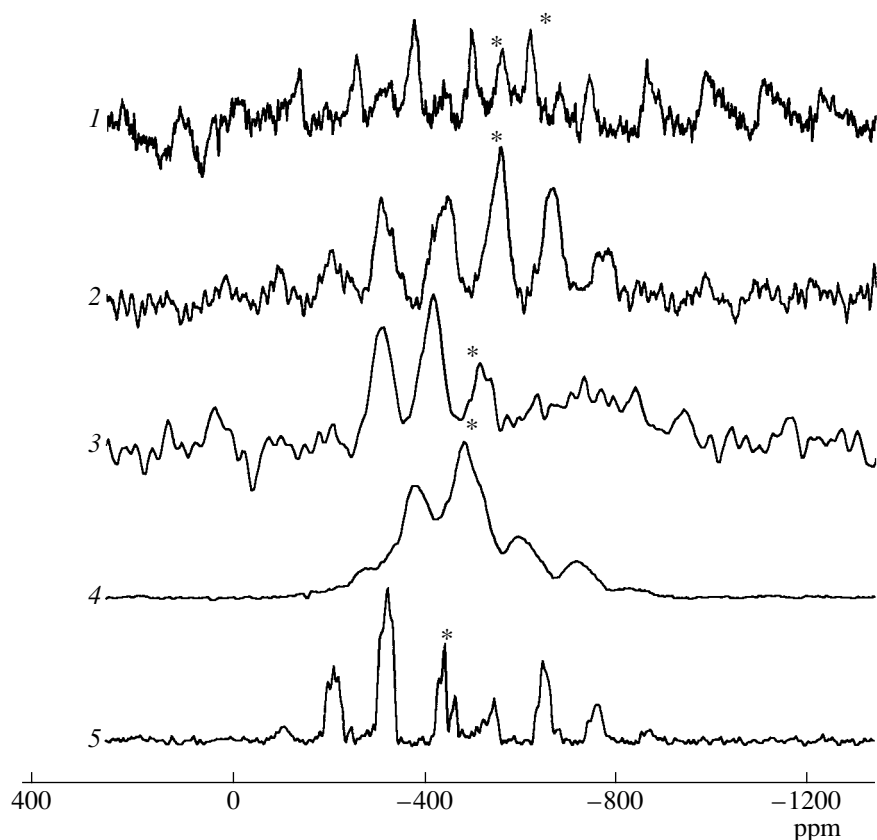
Complex	$\sigma_1$ , ppm	$\sigma_2$ , ppm	$\sigma_3$ , ppm	$\sigma_{\text{iso}}$ , ppm	$C_Q$ , MHz	$\eta_Q$	$\alpha$ , deg	$\beta$ , deg	$\gamma$ , deg
VOCl <sub>3</sub> , –196°C***	$160 \pm 5$	$150 \pm 5$	$-330 \pm 5$	$-6.7 \pm 1$	$5.7 \pm 0.3$	$\sim 0.9$	–	$20 \pm 10$	–
(≡SiO)VOCl <sub>2</sub>	$123 \pm 5$	$354 \pm 5$	$405 \pm 5$	$295 \pm 1$	$1.1 \pm 0.1$	$0.86 \pm 0.02$	$90 \pm 5$	$20 \pm 5$	$80 \pm 5$
(≡SiO) <sub>3</sub> VO****	450	470	1190	710	–	–	–	–	–
(≡SiO) <sub>3</sub> VO · 2H <sub>2</sub> O****	250	330	1200	580	–	–	–	–	–
VOCl <sub>3</sub> /SiO <sub>2</sub> (CCl <sub>4</sub> )	$160 \pm 50$	$515 \pm 10$	$800 \pm 25$	$490 \pm 5$	$\leq 11$	0.10	–	–	–
VOCl <sub>3</sub> /SiO <sub>2</sub> (SiCl <sub>4</sub> ) V <sub>1</sub>	$160 \pm 50$	$515 \pm 10$	$800 \pm 25$	$490 \pm 5$	$\leq 11$	0.10	–	–	–
	$200 \pm 20$	$300 \pm 20$	$1270 \pm 20$	$590 \pm 5$	$\leq 13$	0.15	–	–	–
VOCl <sub>3</sub> /MgCl <sub>2</sub>	$234 \pm 5$	$374 \pm 5$	$830 \pm 5$	$470 \pm 5$	$\leq 13.5$	0.10	–	–	–
Rb <sub>2</sub> VOCl <sub>5</sub> · H <sub>2</sub> O V <sub>1</sub>	$206 \pm 5$	$208 \pm 5$	$814 \pm 5$	$410 \pm 5$	$10 \pm 0.7$	0.001	–	25	–
	$329 \pm 5$	$349 \pm 5$	$640 \pm 5$	$440 \pm 5$	$\leq 12$	0.10	–	–	–

\* The nuclear quadrupole moment  $eQ$  and main values of the electric field gradient tensor ( $V_1, V_2$ , and  $V_3 = eq$ ) are related to  $C_Q$  and  $\eta_Q$  by the formulas  $C_Q = e^2qQ/h$ ;  $V_1 = 1/2(-1 - \eta_Q)V_3$ ;  $V_2 = 1/2(-1 + \eta_Q)V_3$ .

\*\* The main values of the magnetic shielding tensor are related to the parameters  $\delta_{\sigma}, \eta_{\sigma}$ , and  $\sigma_{\text{iso}}$  as  $\sigma_1 = 1/2\delta_{\sigma}(-1 - \eta_{\sigma}) + \sigma_{\text{iso}}$ ;  $\sigma_2 = 1/2\delta_{\sigma}(-1 + \eta_{\sigma}) + \sigma_{\text{iso}}$ ;  $\sigma_3 = \delta_{\sigma} + \sigma_{\text{iso}}$ .

\*\*\* Data from [23].

\*\*\*\* Data from [42].



**Fig. 1.** MAS  $^{51}\text{V}$  NMR spectra ( $\nu_r = 15$  kHz) of the samples: (1)  $\text{VOCl}_3/(\text{SiO}_2, \text{ modified with } \text{SiCl}_4)$ ; (2)  $\text{VOCl}_3/(\text{SiO}_2, \text{ modified with } \text{CCl}_4)$ ; (3)  $\text{VOCl}_3/\text{MgCl}_2\text{-1}$ ; (4)  $\text{Rb}_2\text{VOCl}_5 \cdot 2\text{H}_2\text{O}$  ( $V_2$ ) (delay between pulses 0.1 s); and (5)  $\text{Rb}_2\text{VOCl}_5 \cdot 2\text{H}_2\text{O}$  ( $V_1$ ) (delay between pulses 10 s). The isotropic shift is designated by asterisks.

spectrum has a well-resolved hyperfine structure. Based on the ratio of  $g$  factors of the  $\text{VOCl}_3/\text{MgCl}_2\text{-2}$  sample ( $g_{\parallel} < g_{\perp}$ ), we may conclude that the coordination environment of vanadium, in this case, is probably octahedral with strong tetragonal compression due to the high valence of an axial vanadyl bond  $\text{V}=\text{O}$  [36, 37].

In the case of the  $\text{VOCl}_3/\text{MgCl}_2\text{-1}$  sample, the ESR spectrum containing a broad signal with the unresolved hyperfine structure is also observed, indicating the reduction of some vanadium atoms in this sample.

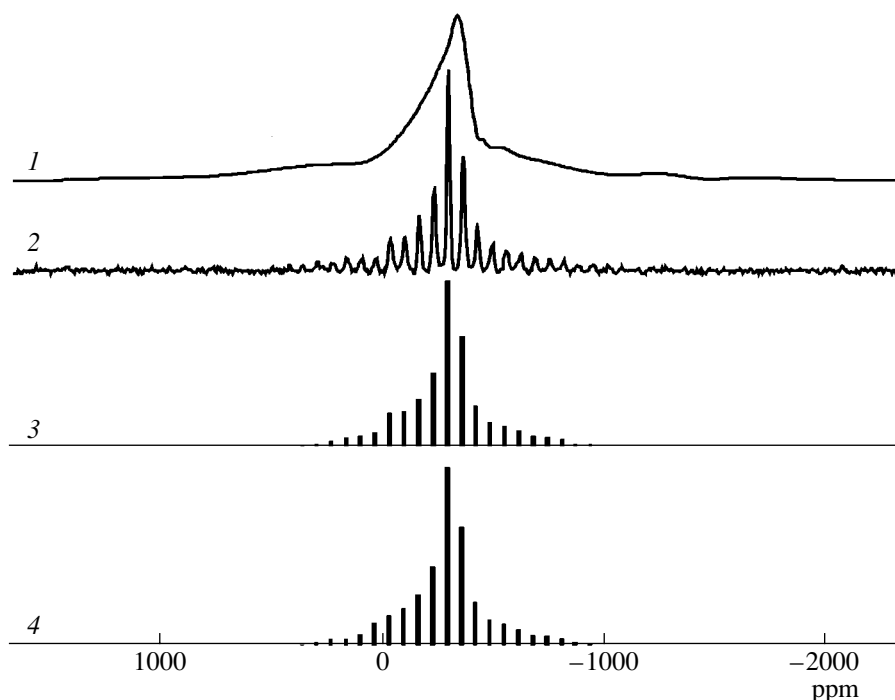
The reduction of vanadium impedes the recording of  $^{51}\text{V}$  NMR spectra. The presence of a paramagnetic  $\text{V}^{4+}$  ion in the immediate vicinity of the pentavalent vanadium atom prevents the detection of the NMR signal from  $\text{V}^{5+}$  due to the broadening effect of these paramagnetic cations. For the same reason we failed to detect the ESR spectrum of the most part of vanadium ions due to the broadening dipole-dipole interaction in the clusters of the  $\text{V}^{4+}$  compounds formed in the  $\text{VCl}_4/\text{MgCl}_2\text{-2}$  catalyst [3]. Therefore, when considering the state of vanadium ions using ESR data, it is necessary to take into account that this interpretation is relevant to only a small fraction of vanadium ions that exist on the surface in the form of isolated  $\text{V}^{4+}$  ions [3].

We estimated the concentration of  $\text{V}^{4+}$  ions in  $\text{VOCl}_3/\text{MgCl}_2\text{-1}$  (~10% of the total concentration of vanadium in the sample) and  $\text{VOCl}_3/\text{MgCl}_2\text{-2}$  (~50%, respectively). Note that, according to [38], the XPS data suggest that approximately a half of vanadium remains in the pentavalent state on the  $\text{VOCl}_3/\text{MgCl}_2\text{-2}$  surface. This suggests that we failed to detect the  $^{51}\text{V}$  NMR spectrum for the  $\text{VOCl}_3/\text{MgCl}_2\text{-2}$  sample because the concentration of  $\text{V}^{4+}$  in the  $\text{VOCl}_3/\text{MgCl}_2\text{-2}$  sample was higher than that in  $\text{VOCl}_3/\text{MgCl}_2\text{-1}$ . The reason for the easy transformation of some surface compounds of  $\text{V}^{5+}$  into  $\text{V}^{4+}$  in the case of the  $\text{MgCl}_2\text{-2}$  support remains unclear.

Nevertheless, despite the reduction of some vanadium ions, we recorded the MAS  $^{51}\text{V}$  NMR spectrum for the  $\text{VOCl}_3/\text{MgCl}_2\text{-1}$  sample in which this side reaction occurs to a lesser degree.

To discuss possible structures of the surface  $\text{V}^{5+}$  compounds in  $\text{VOCl}_3/\text{MgCl}_2\text{-1}$ , we considered additional data for  $\text{VOCl}_3$  supported on hydroxylated silica gel and modified  $\text{SiO}_2$  in which surface OH groups are replaced with chlorine atoms.

The interaction of  $\text{VOCl}_3$  vapor with  $\text{SiO}_2$  results in the reaction with the surface hydroxyl groups



**Fig. 2.** (1) Static and (2) MAS ( $\nu_r = 15$  kHz)  $^{51}\text{V}$  NMR spectra of the  $\text{VOCl}_3/\text{SiO}_2$  samples, (3) spectrum of the intensities of rotation satellites, and (4) theoretical spectrum of intensities of rotation satellites.

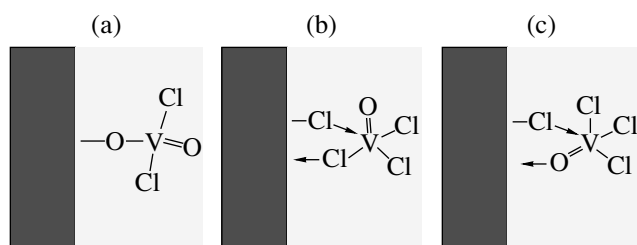


According to published data, only one chlorine atom in the  $\text{VOCl}_3$  molecule is replaced in this reaction [39]. This also follows from the  $^{51}\text{V}$  NMR spectra that exhibit a line with the axial anisotropy of the magnetic shielding tensor with an isotropic chemical shift of  $-295$  ppm (Fig. 2), which is characteristic of  $(\equiv\text{SiO})\text{VOCl}_2$ . Rehder [40, 41] showed that the successive replacement of Cl atoms in a  $\text{VOCl}_3$  molecule by OR groups is manifested in the  $^{51}\text{V}$  NMR spectrum as an additive shift of the signal to a strong field (the chemical shifts range from  $-290$  to  $-310$  ppm for  $\text{VOCl}_2(\text{OR})$ , from  $-410$  to  $-540$  ppm for  $\text{VOCl}(\text{OR})_2$ , and from  $-440$  to  $-710$  ppm for  $\text{VO}(\text{OR})_3$ ). This should also be valid for supported complexes. For example, for the silica gel-supported vanadium atom bound to the surface by three  $(\equiv\text{SiO})_3\text{VO}$  bonds, the isotropic chemical shift is equal to  $-710$  ppm [41]. It is interesting that the hydrated form of this complex has an isotropic shift of  $-580$  ppm, which can be due to either additional coordination of vanadium by water molecules or a decrease in the number of bonds of vanadium with the support surface [42].

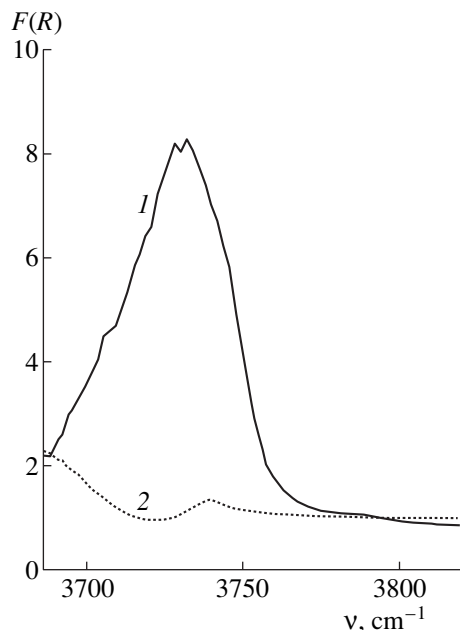
Comparison of the data in Table 2 suggests that the observed spectrum with an isotropic shift of  $-295$  ppm belongs to the vanadium complex immobilized on the support via one  $(\equiv\text{SiO})\text{VOCl}_2$  bond. SATRAS analysis [29] of lateral band intensities in the spectra recorded at different rotation rates provided us with the first reliable estimates for the magnetic shielding tensor and

quadrupole interaction parameters and the mutual tensor orientation for this complex. The spectrum of the intensities of the rotation satellites obtained from the experimental spectrum is shown in Fig. 2, and the theoretical spectrum of the intensities of rotation satellites is presented below. The experimental and theoretical spectra agree well with each other. The magnetic shielding tensor and quadrupole interaction parameters characterize the local environment of vanadium in this complex as a distorted tetrahedron ( $\Delta\sigma < 300$  ppm). The low quadrupole constant (1.1 MHz) indicates the gradient of electric field is small at the site of vanadium. This gradient is created by the local environment of the nucleus and, most likely, can result from the symmetrical arrangement of chlorine atoms in the complex. The absence of axial symmetry (with the symmetry axis along the  $\text{V}=\text{O}$  bond) is most probably due to the deviation of the  $\text{SiO}-\text{V}=\text{O}$  angle from  $180^\circ$ . Figure 3a presents the model of the resulting complex.

The system obtained by the immobilization of  $\text{VOCl}_3$  on modified  $\text{SiO}_2$  in which surface OH groups are replaced by Cl atoms is closer in its composition to the  $\text{VOCl}_3/\text{MgCl}_2$ -1 catalyst. Chlorinated  $\text{SiO}_2$  was prepared using  $\text{CCl}_4(\text{SiO}_2(\text{CCl}_4))$  or  $\text{SiCl}_4(\text{SiO}_2(\text{SiCl}_4))$  as a chlorinating agent [43]. Figures 4 and 5 present the IR spectra of silica gel before and after chlorination. It is seen that OH groups are almost completely removed when these chlorinating agents are used. This is indicated by a considerable decrease in the intensity of the absorption band at  $3740\text{ cm}^{-1}$  that characterizes stretching vibrations of surface OH groups [44–46]. Note that



**Fig. 3.** Vanadium complexes formed in the systems: (a)  $\text{VOCl}_3/\text{SiO}_2$ ; (b) and (c)  $\text{VOCl}_3/(\text{SiO}_2$ , modified with  $\text{CCl}_4$  or  $\text{SiCl}_4$ ) and  $\text{VOCl}_3/\text{MgCl}_2$ .



**Fig. 4.** IR spectra of samples: (1) initial  $\text{SiO}_2$  calcined at  $300^\circ\text{C}$  and (2)  $\text{SiO}_2$  modified with  $\text{CCl}_4$  at  $450^\circ\text{C}$ .

a much smaller amount of vanadium is adsorbed on the chlorinated  $\text{SiO}_2$  surface as compared to the  $\text{VOCl}_3/\text{MgCl}_2$  system (see Table 1).

When  $\text{VOCl}_3$  is supported on the chlorinated  $\text{SiO}_2$  surface, the MAS  $^{51}\text{V}$  NMR spectra (Fig. 1, curves 1 and 2) exhibit a line with an isotropic chemical shift of  $-490$  ppm (when  $\text{CCl}_4$  is used as a chlorinating agent) and two lines with isotropic shifts of  $-490$  and  $-590$  ppm (when  $\text{SiCl}_4$  is used). The characteristic signal from  $(\equiv\text{SiO})\text{VOCl}_2$  with a chemical shift of  $-295$  ppm is absent from both spectra. It is most likely that the second signal  $V_2$  with an isotropic shift of  $-590$  ppm in the spectrum of the  $\text{VOCl}_3/\text{SiO}_2(\text{SiCl}_4)$  sample belongs to a hydrated complex formed when the sample was loaded into the rotor (this is indicated by similarity in NMR spectral parameters for this signal and a signal from the hydrated  $(\equiv\text{SiO})_3\text{VO} \cdot 2\text{H}_2\text{O}$  sample (see Table 2).

Similar MAS  $^{51}\text{V}$  NMR spectral data for the  $\text{VOCl}_3/\text{MgCl}_2$  sample and  $\text{VOCl}_3/\text{SiO}_2(\text{SiCl}_4)$  and  $\text{VOCl}_3/\text{SiO}_2(\text{CCl}_4)$  samples suggest the structures of vanadium complexes in these systems are close. Taking into account a tendency of vanadium to form the  $[\text{VOCl}_4]^-$  complexes and its ability to complete its coordination sphere to pentahedron or octahedron [47], it is reasonable to assume the formation of vanadium complexes with four chlorine atoms in the coordination sphere (one chlorine atom bound to the support completes the coordination sphere of vanadium to a pentahedron). Vanadium complexes of this type ( $\text{M}_2\text{M}'\text{OCl}_5$ -type compounds ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ;  $\text{M}' = \text{V}, \text{Nb}, \text{Cr}, \text{Mo}, \text{W}$ )) are described in [48, 49]. According to these data, vanadium in the  $\text{M}_2\text{M}'\text{OCl}_5$  compounds has a distorted octahedral environment consisting of four chlorine atoms and an oxygen atom in the first coordination sphere, and the sixth position is due to the removed chlorine atom. The corresponding crystal hydrates in which water molecules link vanadium–oxygen–chlorine polyhedra have similar structures [50]. Figure 1 presents the spectrum for one of them,  $\text{Rb}_2\text{VOCl}_5 \cdot \text{H}_2\text{O}$  (curves 4 and 5). It is interesting that the crystal hydrate contains vanadium atoms of two types characterized by different relaxation times. A narrow line with a long relaxation time most likely corresponds to the vanadium atoms in the octahedral coordination  $[\text{VOCl}_4(\text{Cl})]^{2-}$  remote from water molecules (Fig. 1, curve 5), whereas the broadened spectrum with short relaxation times probably corresponds to the  $[\text{VOCl}_4(\text{Cl})]^{2-}$  octahedra located near water molecules (Fig. 1, curve 4).

The spectra of  $\text{Rb}_2\text{VOCl}_5 \cdot \text{H}_2\text{O}$ , supported  $\text{VOCl}_3/\text{MgCl}_2$  samples, and  $\text{VOCl}_3/\text{SiO}_2(\text{SiCl}_4, \text{CCl}_4)$  samples are similar. The apparent differences in the isotropic chemical shift and magnetic shielding tensor can be due to the absence of the rubidium cation that affects the nearest coordination environment of vanadium supported on the magnesium chloride and modified silica gel surfaces.

Perhaps the NMR spectra of the  $\text{VOCl}_3/\text{MgCl}_2$  and  $\text{VOCl}_3/\text{SiO}_2(\text{SiCl}_4, \text{CCl}_4)$  samples differ due to the interaction of  $\text{VOCl}_3$  with the coordinatively unsaturated surface sites of different types. In the case of  $\text{MgCl}_2$ , these surface sites most likely are magnesium ions with chlorine vacancies, and for  $\text{SiO}_2$  the sites are silicon ions with chlorine vacancies (the scheme of this interaction is shown in Figs. 3b and 3c).

The formation of complexes of this type is possible because a  $\text{VOCl}_3$  molecule readily adds the chlorine ion to form  $[\text{VOCl}_4]^-$  or  $[\text{VOCl}_3(\text{Cl})]^-$  complexes [47] and because the interaction of coordinatively unsaturated magnesium or silicon ions with oxygen (complex c in Fig. 3) or chlorine (complex b) of the  $\text{VOCl}_3$  molecule is possible.

Based on  $^{27}\text{Al}$  NMR data, Potapov [51] assumed the formation of similar complexes for aluminum in the  $\text{AlEt}_{3-n}\text{Cl}_n/\text{MgCl}_2$  system.

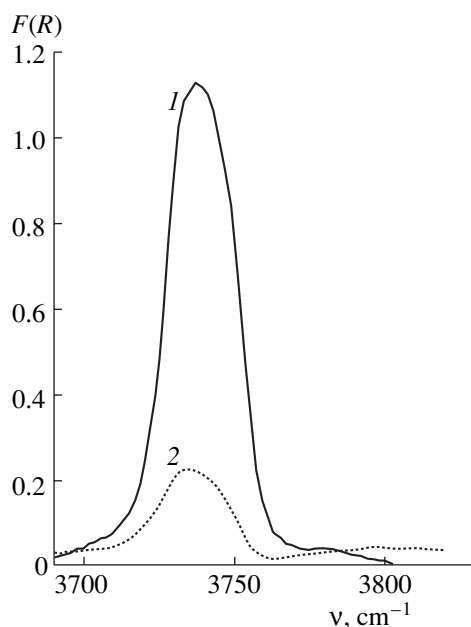


Fig. 5. IR spectra of samples: (1) initial  $\text{SiO}_2$  calcined at  $700^\circ\text{C}$  and (2)  $\text{SiO}_2$  modified with  $\text{SiCl}_4$  at  $450^\circ\text{C}$ .

The structures of surface vanadium compounds proposed in this work agree with the structures of surface paramagnetic  $\text{V}^{4+}$  compounds presented in the review [52] on the basis of ESR data.

## CONCLUSION

Thus, we conclude that the structurally close complexes of pentavalent vanadium with vanadium in the distorted pentahedral environment bound to the support by either two chlorine atoms (Fig. 3, structure b) or chlorine and oxygen atoms (Fig. 3, structure c), can be formed on the  $\text{MgCl}_2$ -1 and chlorinated  $\text{SiO}_2$  surfaces. The high quadrupole constant for the complexes of this type (Table 2) attracted our attention. It is interesting that similar values of the quadrupole constant for the supported vanadium oxide catalysts were observed only for tightly bound forms and explained by the substantial distortion of the local environment of vanadium due to the incorporation of the vanadium octahedra into the near-surface layers of anatase [53].

Although the structures of vanadium compounds on the  $\text{MgCl}_2$  and  $\text{SiO}_2$  surfaces are close, the activity of the silica gel-supported samples is lower (compare rows 1 and 3 with rows 4–6 in Table 1). This fact points to the high efficiency of the  $\text{MgCl}_2$  support.

When choosing between structures b and c presented in Fig. 3, one should take into account the results of comparison of the catalytic properties of the  $\text{VOCl}_3/\text{MgCl}_2$ -2 and  $\text{VCl}_4/\text{MgCl}_2$ -2 systems. Along with the same level of the catalytic activity (rows 5 and 6 in Table 1), these two catalysts manifest several similar properties. When excess  $\text{VCl}_4$  or  $\text{VOCl}_3$  is sup-

ported on  $\text{MgCl}_2$ -2 at  $20^\circ\text{C}$ , the same amount of vanadium chlorides (~1 wt % vanadium [3], also see Table 1) is strongly adsorbed on the support surface. Polyethylenes with close molecular weights and broad (and virtually equivalent) molecular-weight distributions are formed on these catalysts [7, 10]. In addition, these catalysts have the same reactivity in chain transfer with hydrogen used as a regulator of the molecular weight [7]. In the case of ethylene copolymerization with  $\alpha$ -olefins, these catalysts exhibited close copolymerization constants  $r_1$  [10, 12]. The array of these factors suggests that the oxidation states and coordination environments of vanadium in the active sites of VMC obtained from  $\text{VCl}_4$  and  $\text{VOCl}_3$  are close. This implies that the structure in which a vanadium atom is bound to the support surface via two chlorine atoms (Fig. 3b) is the most probable precursor of the active site on the  $\text{VOCl}_3/\text{MgCl}_2$  catalyst surface. The same structure is evidently formed in the case of the  $\text{VCl}_4/\text{MgCl}_2$  catalyst. It is known that further formation of active sites in these systems occurs during the alkylation and reduction of the surface vanadium compounds by an organoaluminum cocatalyst. In the case of the  $\text{VOCl}_3/\text{MgCl}_2$ -2 catalyst, the interaction with the organoaluminum cocatalyst perhaps involves the vanadyl bond  $\text{V}=\text{O}$  in structure b in Fig. 3. After the interaction with the organoaluminum cocatalyst, similar in composition and structure active sites (probably, the alkylated surface compounds of  $\text{V}^{2+}$  or  $\text{V}^{3+}$  in the chlorine environment) are formed on both types of the catalysts ( $\text{VOCl}_3/\text{MgCl}_2$  and  $\text{VCl}_4/\text{MgCl}_2$ ).

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